

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-293241

(43)Date of publication of application : 26.10.1999

(51)Int.Cl.

C09K 11/56
C09K 11/08

(21)Application number : 10-105030

(71)Applicant : SONY CORP

(22)Date of filing : 15.04.1998

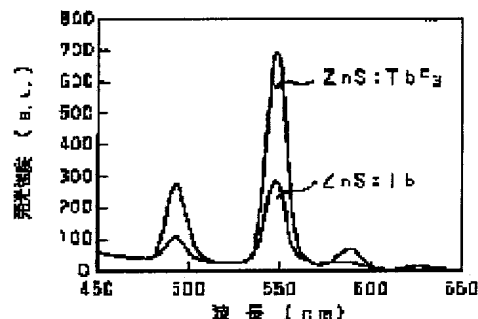
(72)Inventor : IHARA MASARU
KUSUKI TSUNEO
ONO KATSUTOSHI

(54) PHOSPHOR AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a nano-crystalline phosphor which can be excited at a low voltage and fluoresces a green or red color.

SOLUTION: There is provided a nano-crystalline phosphor comprising a nano-structure crystal comprising a fluorine-charge-compensated terbium or europium-activated zinc sulfide and having a particle diameter of 2-5 nm. To produce the nano-crystalline phosphor, zinc acetate and sodium sulfide, terbium nitrate (or europium nitrate), and sodium fluoride are mixed in such amounts that the terbium (or europium) is present in an amount of 0.5-5 mol.% based on the zinc, and the fluorine is present in an amount of 1.5-15 mol.%, and the mixture is subjected to a liquid-phase reaction to coprecipitate nano-structure crystals of zinc sulfide doped with a fluorine-charge-compensated terbium (or europium). By compensating the difference between the charges of terbium or europium and zinc by introducing fluoride ions, the luminance characteristics can be markedly improved.



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CLAIMS

[Claim(s)]

[Claim 1]A fluorescent substance consisting of zinc sulfide activated by terbium by which charge compensation was carried out with fluoride, and consisting of particle diameter of not less than 2 nm, and a nano structure crystal of 5 nm or less.

[Claim 2]The fluorescent substance according to claim 1 being activated by TbF₃.

[Claim 3] A fluorescent substance consisting of zinc sulfide activated with europium by which charge compensation was carried out with fluoride, and consisting of particle diameter of not less than 2 nm, and a nano structure crystal of 5 nm or less.

[Claim 4] The fluorescent substance according to claim 1 being activated by EuF_3 .

[Claim 5] A terbium in a solvent zinc acetate and a sodium sulfide, and a terbium nitrate and sodium fluoride to zinc 0.5–5–mol %, A manufacturing method of a fluorescent substance mixing and carrying out liquid phase reaction at a rate that fluoride will be 1.5–15–mol %, and making a nano structure crystal of zinc sulfide in which a terbium by which charge compensation was carried out with fluoride was doped coprecipitate.

[Claim 6] Europium in a solvent zinc acetate and a sodium sulfide, and nitric acid europium and sodium fluoride to zinc 0.5–5–mol %, A manufacturing method of a fluorescent substance mixing and carrying out liquid phase reaction at a rate that fluoride will be 1.5–15–mol %, and making a nano structure crystal of zinc sulfide in which a terbium by which charge compensation was carried out with fluoride was doped coprecipitate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a fluorescent substance and a manufacturing method for the same.

In particular, it is related with what is called a nano crystal fluorescent substance and a manufacturing method for the same.

[0002]

[Description of the Prior Art] In recent years, in II–VI group semiconductors represented by Si, germanium, etc., such as an ultrafine particle and porous silicon, that the nano structure crystal shows the specific optical characteristic attracts attention. Here, a nano structure crystal means the thing of a crystal grain which has the particle diameter of about several nanometers, and it is generally called a nano crystal.

[0003] In II–VI group semiconductor, when the case where it has a structure crystal of the case where it has the nano structure crystal which was mentioned above, and bulk state is compared, and it has a nano structure crystal, good light absorption characteristics and luminescent characteristic are shown. With II–VI group semiconductor which has a nano structure crystal, since a quantum size effect is revealed, this is considered because it has a bigger band gap than the case where it is a crystal structure of bulk state. That is, in II–VI group semiconductor which has a nano structure crystal, it is thought that a band gap can extend according to a quantum size effect.

[0004] Various fluorescent substances are used for the display of television etc.

Until now, the fluorescent substance used for this kind of display is compounded by calcinating a raw material at an elevated temperature.

And the particle diameter of the compounded fluorescent substance is about (3–10 micrometers)

several micrometers.

[0005]On the other hand in the field of television etc., slimming down of the display is desired in recent years. The plasma display (PDP is called hereafter.), field emission display (FED is called hereafter.), and electroluminescence display (ELD is called hereafter.) which are lightweight flat displays attract attention.

[0006]

[Problem(s) to be Solved by the Invention]By the way, although minuteness making of the electron emission source (cathode) which emits an electron beam is carried out and it is slimmed down for example, especially by the above-mentioned FED which attracts attention, the minuteness making of such an electron emission source makes the voltage of an electron beam fall substantially.

[0007]And in the display on which the voltage of the electron beam fell with this slimming down, when the fluorescent substance whose particle diameter which was mentioned above is about several micrometers is used, although the voltage of an electron beam is low therefore, there is a problem that light is not fully emitted.

[0008]Since the crystal of the conventional fluorescent substance is large, this is considered that the irradiated electron beam is because even the portion into which a fluorescent substance emits light cannot be reached.

[0009]Therefore, in order to realize the above-mentioned FED, the fluorescent substance which can be excited by the low voltage is required.

[0010]Also in the field of CRT, highly minute-ization is advanced increasingly and the more detailed fluorescent substance is demanded. Also in the field of ELD, the fluorescent substance whose luminous efficiency is still higher is demanded.

[0011]The expectation for II-VI group semiconductor which has the nano structure crystal which was mentioned above as a fluorescent substance which fulfills such terms and conditions is high.

[0012]The actual condition is that what is put in practical use until now as a photogen which can be excited by the low voltage has at least ZnO:Zn.

[0013]Although above-mentioned ZnO:Zn carries out copper rust color coloring and II-VI group semiconductor which has a nano crystal structure in which it colors by other colors is just going to be required, The manufacturing method of II-VI group semiconductor which has a nano crystal structure is not fully examined, and the fluorescent substance which has sufficient characteristic is not necessarily obtained.

[0014]This invention is proposed in view of such the conventional actual condition, and can be excited by the low voltage, and an object of this invention is to provide the manufacturing method further for the purpose of providing the fluorescent substance which has a nano crystal structure which emits light in green or red.

[0015]

[Means for Solving the Problem]This invention persons are activating zinc sulfide with a terbium or europium, as a result of repeating various examination about a nano crystal fluorescent substance, By using liquid phase reaction using that a fluorescent substance which emits light in green and red is obtained, that luminous efficiency improves by leaps and bounds by carrying out charge compensation with fluoride in the case of activation, and not the usual solid phase reaction but coprecipitation, It finds out that these nano crystals can be manufactured stably etc., and came to complete this invention.

[0016]That is, a fluorescent substance of this invention consists of zinc sulfide activated with a terbium or europium by which charge compensation was carried out with fluoride, and consists of particle diameter of not less than 2 nm, and a nano structure crystal of 5 nm or less.

[0017]In a solvent a manufacturing method of this invention Zinc acetate and a sodium sulfide, and a terbium nitrate (or nitric acid europium), A terbium (or europium) sodium fluoride to zinc 0.5-5-mol %, Liquid phase reaction is mixed and carried out at a rate that fluoride will be 1.5-15-mol %, and a nano structure crystal of zinc sulfide in which a terbium (or europium) by which charge compensation was carried out with fluoride was doped is made to coprecipitate.

[0018]A zinc sulfide nano crystal activated by a terbium shows green luminescence and an afterglow, and a zinc sulfide nano crystal activated with europium shows red luminescence and an afterglow. At this time, by introducing F^- ion, a difference of an electric charge with a terbium, europium, and zinc is compensated, and a luminescent characteristic improves substantially.

[0019]A nano crystal which has the particle diameter of about 3 nm and was excellent in a luminescent characteristic can be obtained by using not high temperature firing of a raw material like before, i.e., solid phase reaction, but liquid phase reaction using coprecipitation when manufacturing.

[0020]

[Embodiment of the Invention]The fluorescent substance of this invention consists of zinc sulfide activated with a terbium or europium, and consists of a nano structure crystal (nano crystal) with a particle diameter of 2 nm – 5 nm.

[0021]When these are doped by zinc sulfide, using a terbium (Tb), europium (Eu), and also fluoride (F) as an activator, it comes to have peculiar luminescence. For example, the zinc sulfide activated by Tb or TbF₃ shows green luminescence and afterglow. The zinc sulfide activated by Eu or EuF₃ shows red luminescence and an afterglow. In the following description, it writes "ZnS:Tb". [the zinc sulfide in which Tb was doped, for example]

[0022]The zinc sulfide nano crystal fluorescent substance which doped the activator has a large band gap, as a result of generating an exciton, an electron, and the quantum size effect that can confine an electron hole pair in the range of several nanometers.

[0023]In this invention, although a terbium or not only europium but F⁻ ion is introduced in the case of activation, this is based on the viewpoint of charge compensation. That is, when doping a terbium and europium to zinc sulfide, to zinc being divalent (2+), a terbium and europium are trivalent (3+) and cannot take compatibility. Then, charge compensation of the fluoride which is an anion is introduced and carried out. Thereby, compared with the case where F⁻ ion is not introduced, a luminescent characteristic improves more than twice.

[0024]In order to create the above-mentioned zinc sulfide nano crystal fluorescent substance, when doping the activator mentioned above to zinc sulfide, the liquid phase reaction using coprecipitation is used.

[0025]The liquid phase reaction using this coprecipitation is a reaction which makes the salt which has an atom which faces compounding zinc sulfide in a predetermined solvent, and serves as an activator live together in the system of reaction. It is not necessary to be one kind of atom, and may consist of two or more kinds of atoms as an activator doped at this time.

[0026]When specifically manufacturing ZnS:Tb, it becomes the following liquid phase reactions.

[0027]When manufacturing $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{Tb}(\text{NO}_3)_3 + \text{Na}_2\text{S} \rightarrow \text{ZnS:Tb} + 2\text{CH}_3\text{COONaZnS:TbF}_3$, it becomes the following liquid phase reactions.

[0028]When manufacturing $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{Tb}(\text{NO}_3)_3 + 3 \text{NaF} + \text{Na}_2\text{S} \rightarrow \text{ZnS:TbF}_3 + 2\text{CH}_3\text{COONaZnS:Eu}$, it becomes the following liquid phase reactions.

[0029]When manufacturing $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{Eu}(\text{NO}_3)_3 + \text{Na}_2\text{S} \rightarrow \text{ZnS:Eu} + 2\text{CH}_3\text{COONaZnS:EuF}_3$, it becomes the following liquid phase reactions.

[0030]In the $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{Eu}(\text{NO}_3)_3 + 3 \text{NaF} + \text{Na}_2\text{S} \rightarrow \text{ZnS:EuF}_3 + 2\text{CH}_3\text{COONa}$ book method, an activator is added in liquid phase reaction as a salt, as mentioned above. As a salt which has an atom which serves as an activator at this time, acetate, a nitrate, sulfate, etc. can be mentioned according to the kind of that atom.

[0031]For example in a solvent, specifically Zinc acetate and a sodium sulfide, and a terbium nitrate (or nitric acid europium), A terbium (or europium) sodium fluoride to zinc 0.5–5–mol %, Liquid phase reaction is mixed and carried out at a rate that fluoride will be 1.5–15–mol %, The manufacturing method of the fluorescent substance concerning this invention which makes the nano structure crystal of the zinc sulfide in which the terbium (or europium) by which charge compensation was carried out with fluoride was doped coprecipitate, The zinc sulfide which doped the activator of as [whose particle diameter is about several nanometers] can be manufactured by using the liquid phase reaction using such coprecipitation. The zinc sulfide which doped the activator has a large PANDO gap, as a result of generating an exciton, an electron, and the quantum size effect that can confine an electron hole pair in the range of several nanometers. Therefore, the fluorescent substance in which it got twisted in this invention, and improvement in a ***** luminescent characteristic was attained can be manufactured.

[0032]The reason for having introduced F ion using NaF is based on the viewpoint of charge compensation. Although mentioned later, it is possible to improve more than twice and a luminescent

characteristic from the case where it does not introduce, by introducing F^- ion.

[0033]

[Example] Hereafter, the concrete example which applied this invention is described based on an experimental result.

[0034] $ZnS:TbF_3$ -- the case where Tb is used as an activator is shown first. The manufacturing process of $ZnS:Tb$ is shown below.

[0035] 150 ml of methanol solution (0.133 mol/l) of zinc acetate and 75 ml of methanol solution (0.008 mol/l) of the terbium nitrate were mixed, it agitated for 10 minutes using the magnetic stirrer, and the mixed solution was obtained.

[0036] Subsequently, the above-mentioned mixed solution was added in 60 ml of solution (0.4 mol/l) of the sodium sulfide in the state where it agitated using the magnetic stirrer. And it agitated for 20 minutes still more violently.

[0037] Next, centrifugal separation was performed for 20 minutes at 4000 rpm using the centrifuge. Then, air blasting desiccation of the centrifuged sediment was carried out at 50 ** for 24 hours. And $ZnS:Tb$ was manufactured by grinding the solid substance which carried out air blasting desiccation.

[0038] Here, as for the methanol solution of a terbium nitrate, it is preferred to be added in 12.5 ml - 125 ml. That is, as for Tb, it is preferred to be added to 1 mol of Zn at 0.5-mol % - 5-mol% of a rate, and it is the optimal. [3 mol% of]

[0039] The emission spectrum of optical pumping of above-mentioned nano crystal fluorescent substance $ZnS:Tb$ is shown in drawing 1. The green emission of $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} can observe to 543 nm. An excitation spectrum is shown in drawing 2. It has a peak in 490 nm of 380-nm ****.

[0040] It succeeded in green emission similarly by electron beam pumping. The emission spectrum of electron beam pumping under 5 kV and 20nA conditions is shown in drawing 3. The green emission of $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} can observe to 543 nm like the case of optical pumping.

[0041] Although it turned out that the nano crystal fluorescent substance which emits light in green by using Tb as an activator by the above is obtained next, the case where Tb and F are used as an activator is explained. The manufacturing process of $ZnS:TbF_3$ is shown below.

[0042] First, 150 ml of methanol solution (0.133 mol/l) of zinc acetate and 75 ml of methanol solution (0.008 mol/l) of a terbium nitrate, 75 ml of solution (0.024 mol/(l.)) of sodium fluoride was mixed, it agitated for 10 minutes using the magnetic stirrer, and the mixed solution was obtained.

[0043] Subsequently, the above-mentioned mixed solution was added in 60 ml of solution (0.4 mol/l) of the sodium sulfide in the state where it agitated using the magnetic stirrer. And it agitated for 20 minutes still more violently.

[0044] Next, centrifugal separation was performed for 20 minutes at 4000 rpm using the centrifuge. Then, air blasting desiccation of the centrifuged sediment was carried out at 50 ** for 24 hours. And $ZnS:TbF_3$ was manufactured by grinding the solid substance which carried out air blasting desiccation.

[0045] Here, the ranges of the methanol solution of a terbium nitrate are 12.5 ml - 125 ml, and it is preferred that the solution of sodium fluoride is also added in 12.5 ml - 125 ml. That is, Tb is 0.5-mol % - 5-mol% of a rate to 1 mol of Zn, as for F, it is preferred to be added at 1.5-mol % - 15-mol% of a rate, and 9-mol% of F is [Tb] the optimal 3-mol%.

[0046] The emission spectrum of optical pumping of above nano crystal fluorescent substance $ZnS:TbF_3$ is shown in drawing 4. After all, the green emission of $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} can observe to 543 nm. And about 2.5 times and a luminescent characteristic improved by introducing F^- ion from a viewpoint of charge compensation.

[0047] The case where Eu is used as $ZnS:EuF_3$, next an activator is explained. The manufacturing process of $ZnS:Eu$ is shown below.

[0048] 150 ml of methanol solution (0.133 mol/l) of zinc acetate and 75 ml of methanol solution (0.008 mol/l) of nitric acid europium were mixed, it agitated for 10 minutes using the magnetic stirrer, and the mixed solution was obtained.

[0049] Subsequently, the above-mentioned mixed solution was added in 60 ml of solution (0.4 mol/l) of the sodium sulfide in the state where it agitated using the magnetic stirrer. And it agitated for 20

minutes still more violently.

[0050]Next, centrifugal separation was performed for 20 minutes at 4000 rpm using the centrifuge. Then, air blasting desiccation of the centrifuged sediment was carried out at 50 ** for 24 hours. And ZnS:Eu was manufactured by grinding the solid substance which carried out air blasting desiccation.

[0051]Here, as for the methanol solution of nitric acid europium, it is preferred to be added in 12.5 ml – 125 ml. That is, as for Eu, it is preferred to be added to 1 mol of Zn at 0.5–mol % – 5–mol% of a rate, and it is the optimal. [3 mol% of]

[0052]The emission spectrum of optical pumping of above-mentioned nano crystal fluorescent substance ZnS:Eu is shown in drawing 5. The red light of $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} can observe to 616 nm.

An excitation spectrum is shown in drawing 6. It has a peak in 466 nm of 397–nm ****.

[0053]It succeeded in red light similarly by electron beam pumping. The emission spectrum of electron beam pumping under 5 kV and 20nA conditions is shown in drawing 7. The red light of $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} can observe to 616 nm like the case of optical pumping.

[0054]Although it turned out that the nano crystal fluorescent substance which emits light in red by using Eu as an activator by the above is obtained next, the case where Eu and F are used as an activator is explained. The manufacturing process of ZnS:EuF₃ is shown below.

[0055]First, 150 ml of methanol solution (0.133 mol/l) of zinc acetate and 75 ml of methanol solution (0.008 mol/l) of nitric acid europium, 75 ml of solution (0.024 mol/(l.)) of sodium fluoride was mixed, it agitated for 10 minutes using the magnetic stirrer, and the mixed solution was obtained.

[0056]Subsequently, the above-mentioned mixed solution was added in 60 ml of solution (0.4 mol/l) of the sodium sulfide in the state where it agitated using the magnetic stirrer. And it agitated for 20 minutes still more violently.

[0057]Next, centrifugal separation was performed for 20 minutes at 4000 rpm using the centrifuge. Then, air blasting desiccation of the centrifuged sediment was carried out at 50 ** for 24 hours. And ZnS:EuF₃ was manufactured by grinding the solid substance which carried out air blasting desiccation.

[0058]Here, the ranges of the methanol solution of nitric acid europium are 12.5 ml – 125 ml, and it is preferred that the solution of sodium fluoride is also added in 12.5 ml – 125 ml. That is, Eu is 0.5–mol % – 5–mol% of a rate to 1 mol of Zn, as for F, it is preferred to be added at 1.5–mol % – 15–mol% of a rate, and 9–mol% of F is [Eu] the optimal 3–mol%.

[0059]The emission spectrum of optical pumping of above nano crystal fluorescent substance ZnS:EuF₃ is shown in drawing 8. After all, the red light of $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} can observe to 616 nm.

And about 2.2 times and a luminescent characteristic improved by introducing F⁻ ion from a viewpoint of charge compensation.

[0060]When ZnS:Tb manufactured as mentioned above, ZnS:TbF₃, ZnS:Eu, and ZnS:EuF₃ were analyzed based on the breadth of a transmission electron microscope **** X-ray diffraction peak, particle diameter was about 3 nm in each case.

[0061]Since especially ZnS:TbF₃ and ZnS:EuF₃ have the dramatically outstanding luminescent characteristic, excited light of them can be carried out by the low voltage, they are used as the thin flat-panel display in which the electron beam of the low voltage is used, for example, a fluorescent substance of FED, and are preferred. Of course, it cannot be overemphasized that it is effective also in highly minute CRT or ELD.

[0062]

[Effect of the Invention]According to this invention, it is possible to provide the nano crystal fluorescent substance which emits light in green or red so that clearly also from the above explanation.

[0063]The fluorescent substance which it can improve substantially, is an ultrafine particle called nano size, and can moreover carry out excited light of the luminous efficiency also by the low voltage can be provided by introducing F⁻ ion from a viewpoint of charge compensation especially.

[0064]The fluorescent substance of this invention can be used for FED, highly minute CRT, ELD, etc., and is effective in highly-efficient-izing of these displays.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a characteristic figure showing the emission spectrum of ZnS:Tb.

[Drawing 2]It is a characteristic figure showing the excitation spectrum of ZnS:Tb.

[Drawing 3]It is a characteristic figure showing the emission spectrum in electron beam pumping of ZnS:Tb.

[Drawing 4]It is a characteristic figure comparing and showing the emission spectrum of ZnS:Tb and ZnS:TbF₃.

[Drawing 5]It is a characteristic figure showing the emission spectrum of ZnS:Eu.

[Drawing 6]It is a characteristic figure showing the excitation spectrum of ZnS:Eu.

[Drawing 7]It is a characteristic figure showing the emission spectrum in electron beam pumping of ZnS:Eu.

[Drawing 8]It is a characteristic figure comparing and showing the emission spectrum of ZnS:Eu and ZnS:EuF₃.

[Translation done.]

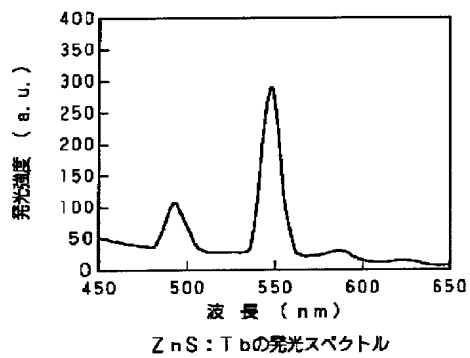
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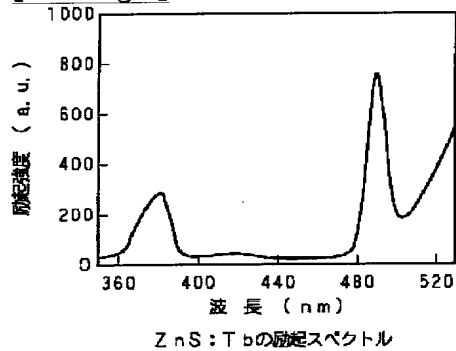
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DRAWINGS

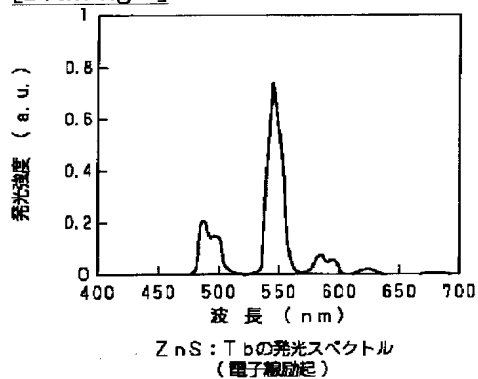
[Drawing 1]



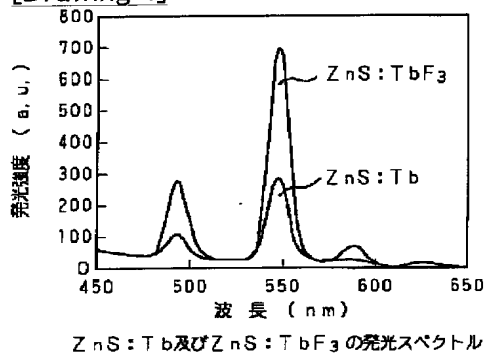
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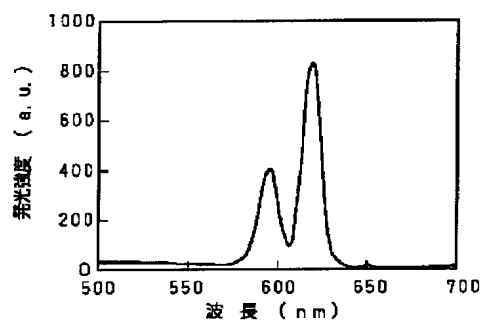
[Drawing 3]



[Drawing 4]

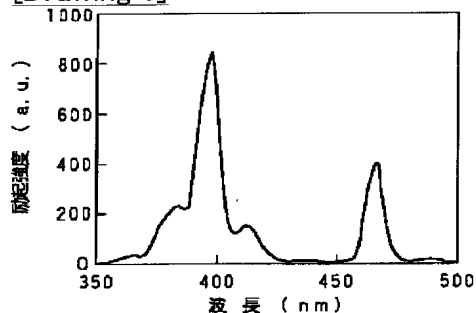


[Drawing 5]



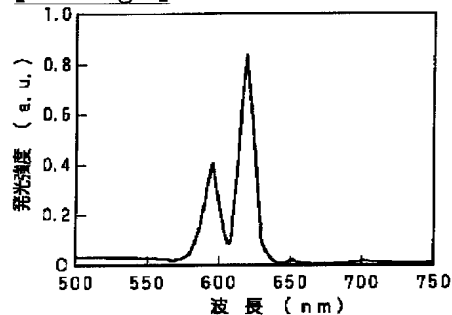
ZnS:Euの発光スペクトル

[Drawing 6]

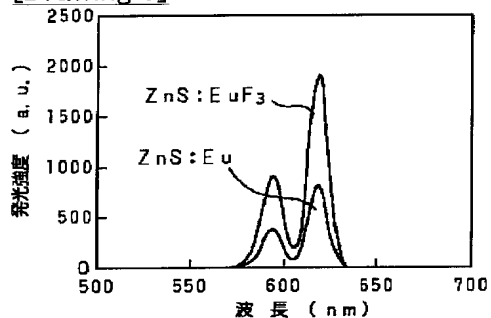


ZnS:Euの発光スペクトル

[Drawing 7]

ZnS:Euの発光スペクトル
(電子線励起)

[Drawing 8]

ZnS:Eu及びZnS:EuF₃の発光スペクトル

[Translation done.]